Relating Differences in Mineral Reaction Rates to Microenvironment Creation and Heterogeneous Pore-Scale Phase Distribution at the Hanford Site

PNNL SFA (Investigators: John M. Zachara; Jim K. Fredrickson)

K. Rosso (PI), A. Felmy, C. Pearce, J. Liu, O. Qafoku, *PNNL*; S. Heald, D. Latta, M. Boyanov, K. Kemner, *ANL;* E. Arenholz, *LBNL;* E. Buck, L. Shi, J. McKinley, D. Moore, T. Resch, T. Schaef, M. Bowden, *PNNL*

This research seeks to unravel effects of mineralogic reactive heterogeneity, local redox and pH gradients, and the resulting distribution of mineralogic and contaminant reaction products in the Hanford subsurface. Hanford sediments are relatively rich in Fe-bearing minerals in the form of magnetite, titanomagnetite, ilmenite, Fe(II)/Fe(III)-phyllosilicates, and Fe(III)-oxides, as well as carbonates, pyroxenes and feldspars. These phases are reactive to different extents with important system species such as O_2, H^+, and Fe(II). These differences in mineral redox reactivity or dissolution rate can generate local microenvironments and a heterogeneous pore-scale mineral or contaminant phase distribution. To investigate these effects, a greater understanding of the reactivity of these phases under dynamic reaction-limited conditions is required.

Towards this goal, natural Fe-rich mineral samples from sediments collected at several locations on Hanford's central plateau were isolated by magnetic separation. This fraction represented ~2 wt% of the total sediment, and was composed of 90% magnetite as determined by XRD. XMP analysis showed that Ti was the most significant impurity, and that these grains could be described with the titanomagnetite formula $Fe_{3-x}Ti_xO_4$ with the dominant composition as $x = 0.15$ by chemical analysis and EPMA in the bulk, and by *L*-edge XAS and XPS at the surface. XMCD showed that octahedral Fe(II) was measurable within 5 nm of the mineral surface. This Fe(II) was highly responsive to the aqueous environment as a result of transitioning from oxic Hanford groundwater to reduced Ringold groundwater. Reaction of magnetically-separated natural phases showed that they are able to reduce Tc(VII) to Tc(IV), and U(VI) to U(IV) with concurrent oxidation of structural Fe(II) to Fe(III), as were synthetic $x = 0.15$ bulk powder and nanoparticle analogue phases developed using EMSL facilities. These studies revealed a wide range of Tc(VII) and U(VI) reduction rates and product form as a function of the Ti content, demonstrating the likelihood for a spatially heterogeneous distribution of products associated with such phases in the subsurface depending on composition. Parallel studies on Pu-containing sediments at the Hanford site that had received high concentrations of acidic waste water showed a complex heterogeneous distribution of precipitates. NanoSims and TEM measurements revealed that these differences were correlated with differences in the basicity of the initially present minerals. Neutralization of the acidic wastes at the reactive mineral surfaces apparently created local higher pH microenvironments that induced precipitation of Pu compounds and other phases selectively at these locations.

Current research is focused on examining relationships between flow, mineral redox and pH neutralization rates, and pore-scale phase distributions. Variations in redox reactivity will be examined by studying the titanomagnetite mineral series with redox probe species (Tc(VII) ,U(VI) and Pu(V)) which are reduced to their insoluble tetravalent state over a broad range of redox potentials. We will also use Fe(II)-oxidizing microbial cytochromes as redox probe species with biogeochemical implications. These studies will be conducted in reaction and microscale flow-through packed porous media, combined with in situ spectroscopic quantification of electron transfer progress and synchrotron-based mapping of chemical and valence distributions.